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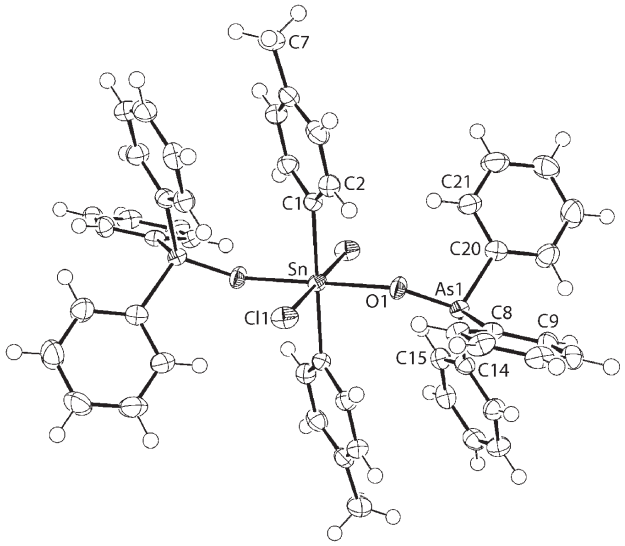
Crystal structure of dichlorido-bis(4-methylphenyl-κ*C*)-bis(triphenylarsine oxide-κ*O*) tin(IV), $C_{50}H_{44}As_2Cl_2O_2Sn$



https://doi.org/10.1515/ncrs-2019-0564
Received August 5, 2019; accepted September 13, 2019; available online October 9, 2019

Abstract

$C_{50}H_{44}As_2Cl_2O_2Sn$, monoclinic, $P2_1/n$ (no. 14), $a = 10.84633(6)$ Å, $b = 14.61376(9)$ Å, $c = 13.53951(8)$ Å, $\beta = 91.5073(6)°$, $V = 2145.35(2)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0237$, $wR_{ref}(F^2) = 0.0642$, $T = 100(2)$ K.

CCDC no.: 1953497

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.12 × 0.08 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	7.91 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	75.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	53250, 4435, 0.046
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4242
$N(param)_{refined}$:	260
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.500000	0.500000	0.500000	0.01384(6)
As1	0.66729(2)	0.43682(2)	0.27777(2)	0.01415(7)
Cl1	0.67033(4)	0.46520(3)	0.62790(4)	0.02160(11)
O1	0.63487(13)	0.48457(10)	0.38594(11)	0.0183(3)
C1	0.54081(18)	0.64306(13)	0.50834(14)	0.0164(4)
C2	0.66148(18)	0.67527(14)	0.51559(15)	0.0190(4)
H2	0.727851	0.634344	0.504885	0.023*
C3	0.6866(2)	0.76639(15)	0.53827(15)	0.0221(4)
H3	0.769732	0.786761	0.542520	0.027*
C4	0.5912(2)	0.82832(14)	0.55485(15)	0.0226(4)
C5	0.4703(2)	0.79716(14)	0.54207(16)	0.0223(4)
H5	0.403890	0.838788	0.549282	0.027*
C6	0.44535(19)	0.70638(14)	0.51899(15)	0.0195(4)
H6	0.362189	0.686955	0.510298	0.023*
C7	0.6166(3)	0.92526(15)	0.58733(19)	0.0315(5)
H7A	0.698620	0.928630	0.619322	0.047*
H7B	0.554282	0.944433	0.634144	0.047*
H7C	0.613581	0.965773	0.529634	0.047*
C8	0.84044(17)	0.41162(13)	0.28661(14)	0.0157(4)
C9	0.90786(18)	0.38482(14)	0.20524(15)	0.0191(4)
H9	0.867494	0.374931	0.143036	0.023*
C10	1.03469(19)	0.37267(15)	0.21592(16)	0.0216(4)
H10	1.081284	0.353547	0.161177	0.026*
C11	1.09292(18)	0.38855(14)	0.30668(17)	0.0220(4)
H11	1.179828	0.381632	0.313395	0.026*
C12	1.02569(19)	0.41440(14)	0.38773(16)	0.0216(4)
H12	1.066592	0.424613	0.449651	0.026*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C13	0.89875(18)	0.42541(13)	0.37871(15)	0.0179(4)
H13	0.852158	0.442090	0.434363	0.022*
C14	0.57945(18)	0.32766(14)	0.24017(14)	0.0171(4)
C15	0.45057(18)	0.32831(14)	0.23835(15)	0.0190(4)
H15	0.406728	0.381678	0.256731	0.023*
C16	0.38777(19)	0.24981(16)	0.20929(15)	0.0226(4)
H16	0.300183	0.248953	0.209012	0.027*
C17	0.4519(2)	0.17227(15)	0.18053(15)	0.0236(4)
H17	0.408065	0.119149	0.159582	0.028*
C18	0.5798(2)	0.17235(15)	0.18236(16)	0.0242(4)
H18	0.623405	0.119221	0.162841	0.029*
C19	0.64437(19)	0.24993(14)	0.21268(16)	0.0212(4)
H19	0.731983	0.249962	0.214649	0.025*
C20	0.63327(18)	0.52586(15)	0.17751(15)	0.0184(4)
C21	0.5851(2)	0.60954(15)	0.20567(17)	0.0249(4)
H21	0.570051	0.621967	0.273153	0.030*
C22	0.5593(2)	0.67492(16)	0.13349(18)	0.0311(5)
H22	0.525401	0.732221	0.151720	0.037*
C23	0.5826(2)	0.65733(17)	0.03550(18)	0.0311(5)
H23	0.565915	0.702814	−0.013171	0.037*
C24	0.6303(2)	0.57329(19)	0.00812(18)	0.0341(5)
H24	0.646414	0.561273	−0.059279	0.041*
C25	0.6545(2)	0.50675(16)	0.07909(18)	0.0276(5)
H25	0.685449	0.448613	0.060436	0.033*

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected. The IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm^{-1}.

Di(4-methylphenyl)tin dichloride was prepared from the comproportionation reaction of tetra(4-methylphenyl)tin using different stoichiometric amounts of stannic chloride [5]. Di(4-methylphenyl)tin dichloride (0.41 g, 1 mmol) and triphenylarsine oxide (Sigma Aldrich; 0.64 g, 2 mmol) were dissolved in ethanol (50 mL) and refluxed for 1 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. The crystals were filtered, washed with a minimum amount of *n*-hexane and air-dried. Yield: 0.25 g (25%). **M.pt:** 479–481 K. **IR** (cm^{-1}) 1085 (m) ν(C—O), 996 (m) ν(As—O), 478 (w) ν(Sn—O).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$.

Comment

Despite the first crystal structure determination of a triorganoarsine oxide adduct of an organotin halide species being reported in 1983, i.e. binuclear $(Ph_3SnCl)O{=}As(Ph_2)CH_2CH_2As(Ph_2){=}O(Ph_3SnCl)$ [6], with five-coordinate tin centres, there have been comparatively few subsequent studies, especially compared to analogous triorganophosphine oxide adducts. While a one-dimensional coordination polymer was observed in the crystal of $\{[(n\text{-}Bu)_2SnCl_2]O{=}As(Ph_2)CH_2CH_2As(Ph_2){=}O[(n\text{-}Bu)_2SnCl_2]\}_n$, with hexa-coordinate tin centres [7], mononuclear, five-coordinate species are evident in the three remaining crystal structures, as exemplified in the structure of $(4\text{-}ClC_6H_4)_2SnCl_2(O{=}AsPh_3)$ [8]. Herein, the crystal and molecular structures of a hexa-coordinate adduct of di(4-methylphenyl)tin dichloride with two molecules of triphenylarsine oxide, $(4\text{-}MePh)_2SnCl_2(O{=}AsPh_3)_2$, (I), are described.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids and unlabelled atoms are related by the symmetry operation (i) $1 - x$, $1 - y$, $1 - z$). The tin atom is located on a crystallographic centre of inversion and is coordinated by two chlorido ligands, two *ipso*-carbon atoms of the 4-methylphenyl substituents and two oxide-oxygen atoms from two $O{=}AsPh_3$ ligands (see the figure). The resulting $C_2Cl_2O_2$ donor set has all like-atoms trans and defines an octahedral geometry. The Sn—Cl1 [2.5500(4) Å], Sn—O1 [2.1667(14) Å] and As—O1 [1.6681(14) Å] bond lengths may be compared with the bond lengths in five-coordinate $Ph_3SnCl(O{=}AsPh_3)$ [9]. Here [9], two independent molecules comprise the asymmetric unit. Even allowing for the increase in coordination number in (I), compared with $Ph_3SnCl(O{=}AsPh_3)$ [9], the Sn—Cl bond lengths [2.613(2) and 2.634(2) Å] in the latter are elongated with respect to (I), as are the Sn—O bonds [2.260(4) and 2.283(4) Å]. These results are directly related to substituting an electronegative chlorido ligand in (I) with another organic substituent (phenyl), which reduces the Lewis acidity of the tin atom. The As—O bonds [1.6681(14) Å cf. 1.663(4) and 1.672(4) Å] in the two structures are similar. Within the molecule, two phenyl rings, tin- and arsenic-bound, align so as to form an intramolecular π···π interaction. Thus, the inter-centroid $Cg(C1{-}C6)\cdots Cg(C14{-}C19)^{i}$ separation = 3.6547(12) Å and the angle of inclination = 6.15(10)°.

The molecular packing in the crystal of (I) features phenyl-C—H···π(phenyl) interactions involving the $Ph_3As{=}O$ phenyl rings [$C22{-}H22\cdots Cg(C8{-}C13)^{ii}$: $H22\cdots Cg(C8{-}C13)^{ii} = 2.54$ Å, $C22\cdots Cg(C8{-}C13)^{ii} = 3.430(2)$ Å with angle at H22 = 155° and $C23{-}H23\cdots Cg(C14{-}C19)^{iii}$: $H23\cdots Cg(C14{-}C19)^{iii} = 2.88$ Å, $C23\cdots Cg(C14{-}C19)^{iii} = 3.726(3)$ Å with angle at H23 = 149° for (ii) $3/2 - x$, $1/2 + y$, $1/2 - z$ and (iii) $1 - x$, $1 - y$, $-z$]. With four such interactions per molecule, a three-dimensional architecture ensues.

The program Crystal Explorer 17 [10] was employed to evalaute the molecular packing further by calculating the Hirshfeld surfaces/two-dimensional fingerprint plots (overall and delineated) for the entire molecule using standard procedures [11]. There are three different types of surface contacts contributing over 98% of all contacts, namely H···H [58.7%], clearly dominant, C···H/H···C [33.1%] and Cl···H/H···Cl [7.0%].

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant No. STR-RCTR-RCCM-001–2019.

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